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Studies In Qualitative Organic Analysis

**STUDIES IN QUALITATIVE ORGANIC
ANALYSIS**

BY

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STUDIES IN QUALITATIVE ORGANIC ANALYSIS

INTRODUCTION

The principal object of this work was to prepare the ortho, meta, and para amino-ethyl-benzenes and certain of their derivatives which were to be used in connection with work in qualitative organic analysis. A means of identification of the rearrangement products of such compounds as the N-alkyl-anilines was especially desired in connection with the study of rearrangements which is being carried on in this laboratory at the present time.

Before taking up the main problem, some preliminary work was done in the preparation of the benzene-sulphonyl derivatives of certain amines, in order to test the methods of separation and purification of such derivatives.

HISTORICAL

Beilstein and Kuhlberg¹ nitrating ethyl-benzene with a mixture of two volumes of fuming and one of concentrated nitric acid, secured a mixture of ortho and para nitro-ethyl-benzenes, which were separated by means of twenty fractional distillations. This tedious separation was necessary because of the fact that the two metamers differed only slightly in boiling points.

Béhal and Choay² using the same method of preparation, secured a mixture of the ortho and para nitro-ethyl-benzenes, which was reduced to the corresponding mixture of amines, and separated by means of the different solubilities in water of the acetyl derivatives of these amines. The melting point of the



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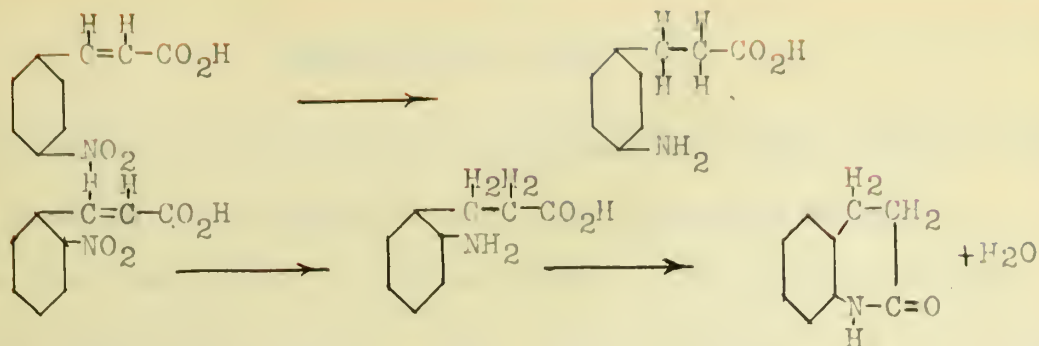
acetyl derivative of the ortho compound is reported at 94°; that of the para at 112°. The free amines were not prepared by them. They report about three-fifths ortho and two-fifths para.

Schultz and Flachsländer³ have also prepared the ortho and para nitro-ethyl-benzenes, and have investigated carefully the conditions necessary to produce a maximum yield. Using a nitric and sulphuric acid mixture, and nitrating at a relatively low temperature followed by a heating on the water or sand bath, it was possible to secure as high as a 94 percent yield of the mixed nitro derivatives. This work is especially valuable because of the great care taken in the separation of the mixture, the latter being subjected to eighty fractional distillations under diminished pressure. In general the work of Beilstein is verified.

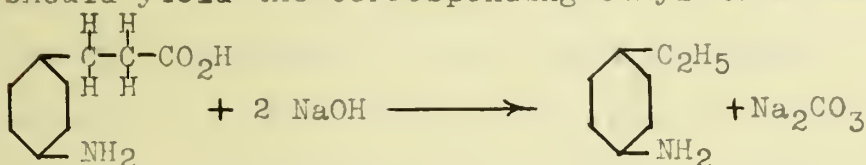
It is of interest to note the relative proportions of the two metamers obtained under various conditions of nitration. Beilstein¹ obtained almost equal amounts of the two products, whereas Schultz and Flachsländer³ obtained two parts of the ortho to one part of the para compound.

THEORETICAL PART

In order to avoid the tedious separation by means of the long continued fractional distillation, a method of preparation of the amino-ethyl-benzenes separately was looked for. It was thought possible to start with nitro-cinnamic acids, and secure by reduction the corresponding amino-hydro-cinnamic acids.



These amino acids were to be fused with soda-lime, a treatment which should yield the corresponding ethyl-amino-benzenes.

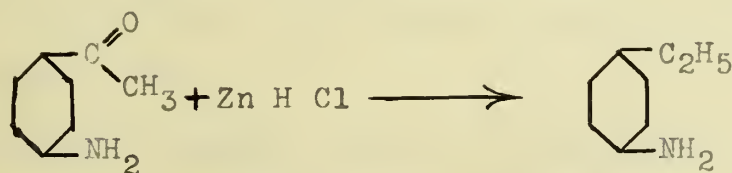


It was thought possible to carry out the reduction of both the nitro group and the unsaturated side chain in one step by using sodium amalgam, or if that failed by a method reported by Stohr⁴ using zinc and hydrochloric acid.

Another possibility considered, was the preparation from the corresponding nitro-bromo-benzenes by means of the Grignard reaction.



Still another possibility⁵ was the reduction of the several amino-aceto-phenones to the corresponding hydrocarbons.



EXPERIMENTAL PART

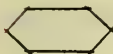
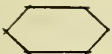
PREPARATION AND PURIFICATION OF BENZENE-SULPHONYL DERIVATIVES.

The method used for the preparation of the benzene-sulphonyl derivatives was that given in Lassar Cohen⁶. The amine suspended in potassium hydroxide solution, was treated with one and one-half times its mass of benzene-sulphonyl chloride, and the whole heated until the excess of benzene-sulphonyl chloride had dissolved. In each case one cubic centimeter of the amine was added to about 16 cubic centimeters of a 12 1/2 percent solution of potassium hydroxide, and two cubic centimeters of the benzene-sulphonyl chloride added slowly. After warming, the alkaline solution was extracted with ether to remove any disulphonyl derivative of the amine which might have formed, and the derivative precipitated by the addition of hydrochloric acid. The derivative was crystallized from a hot solution of dilute alcohol. A fifty percent solution gave the most satisfactory results. The crystallization was repeated five times, but it was found that the melting point of the compounds became constant after the first crystallization.

The melting point of the benzene-sulphonyl derivative of aniline was found to be 108°-109°, which agrees with the value given in the literature. The melting point of the meta-toluidine was found to be 92°-93°. The values reported in the literature range from 80° to 90°.

The Grignard reaction proved to be a failure as the magnesium halide appeared to attack the nitro group. This reaction was known to be possible since the action of magnesium-ethyl-halide on nitro-benzene is discussed in Ahren's Vortrage⁷. The reaction

proceeded vigorously at first but stopped abruptly when about one-half of the para nitro-bromo-benzene had been added to the solution of magnesium-ethyl-bromide.

REDUCTION OF THE NITRO-CINNAMIC ACIDS WITH SODIUM AMALGAM. Ten grams of para nitro-cinnamic acid were dissolved in 75 cubic centimeters of dilute sodium hydroxide solution. The amalgam was added slowly. The reaction proceeded rapidly at first, and the solution began to become cloudy. After 400 grams of three percent sodium amalgam had been added, an additional quantity of 150 grams was powdered, and added at one time. Carbon dioxide was run into the flask, and heat applied. After two hours of heating, the products of reduction consisted of a clear amber colored solution and a yellow compound. The latter, although slightly soluble in hot water, was insoluble in dilute acids, showing the absence of the desired basic compound. It is probable that the product was a sodium salt of this type: $\text{Na-O}_2\text{-C-CH}_2\text{-CH}_2\text{-}$
- $\overset{\text{H}}{\underset{\text{H}}{\text{N}}}\text{-}\overset{\text{H}}{\underset{\text{H}}{\text{N}}}$ -- $\text{CH}_2\text{-CH}_2\text{-CO}_2\text{-Na}$, as it had no definite melting point.

REDUCTION OF PARA NITRO-CINNAMIC ACID WITH TIN AND HYDROCHLORIC ACID. Using the method reported by Stohr⁴, the ethyl ester of the acid was prepared by refluxing for fifteen or twenty minutes, a mixture of 30 grams of para nitro-cinnamic acid and 150 cubic centimeters of absolute ethyl alcohol saturated with dry hydrochloric acid gas. The mixture was allowed to stand for about one hour, and was then poured into water in order to separate the ester. The yield of product was very good since only very slight traces of the sparingly soluble para nitro-cinnamic acid could be detected during the process of purification.

To 30 grams of the ester there were added 120 grams of zinc

and 135 grams of hydrochloric acid, or about three times the theoretical amount of both zinc and acid. The amino acid was isolated as its hydrochloride. The latter was dissolved in potassium hydroxide solution, which upon acidification with acetic acid, gave a white crystalline precipitate melting at 133° . The result confirms Stohr's⁴ report as it might be supposed from the data in the literature that zinc and hydrochloric acid does not reduce the $-C=C-$ group. The yield was rather poor as only one gram was obtained from one-half of the zinc salt.

As a result of these preliminary experiments, it was decided to reduce the nitro-cinnamic acid in two stages.

REDUCTION OF NITRO GROUP WITH FERROUS SULPHATE IN AMMONIACAL SOLUTION⁸. Thirty grams of para nitro-cinnamic acid were dissolved in about 200 cubic centimeters of dilute ammonia. A hot solution of 270 grams of ferrous sulphate in 700 cubic centimeters of water was prepared, and an excess of ammonia added. The hot solution of para nitro-cinnamic acid was poured into the ferrous hydroxide mixture, and the whole digested at 100° for ten minutes. After digestion the mixture was filtered and the filtrate acidified with acetic acid. A heavy yellow precipitate was thrown down. Ten grams of para amino-cinnamic acid was obtained. The process was repeated using 470 grams of ferrous sulphate dissolved in a liter of water, 375 cubic centimeters of dilute ammonia and 50 grams of nitro-cinnamic acid. One-fifth of the solution was reduced at a time in order to see the effect of different conditions upon the yield. One portion digested for five minutes, yielded 5 grams; another portion digested for ten minutes, yielded $7\frac{1}{2}$ grams. From the three remaining portions, which were digested for ten minutes, a total yield of 22 grams was obtained. The

total amount of product obtained was 34 grams out of a theoretical yield of 42 grams. The process was considered rather convenient and satisfactory.

REDUCTION OF THE PARA AMINO-CINNAMIC ACID. The amino-cinnamic acid was reduced with 3 percent sodium amalgam, and the para amino-hydro-cinnamic acid isolated as its hydrochloride, and also as the free acid.

In the first case, 20 grams of the amino-cinnamic acid were placed in a flask with about 75 cubic centimeters of water. Pulverized amalgam was added slowly until the acid dissolved. The remainder of 360 grams of amalgam was added at one time, and carbon dioxide run in to neutralize the excess sodium hydroxide formed. It was necessary to add 180 grams more of the amalgam or an excess of about 200 percent. The reaction was complete in about one hour. The mixture was filtered, acidified with an excess of hydrochloric acid, and the solution evaporated on the steam bath, hydrogen sulphide being run in to prevent oxidation. The solution was finally saturated with hydrogen chloride gas, and filtered from the precipitated sodium chloride. The hydrochloride of the amino compound, which separated out on cooling, was filtered off; the filtrate evaporated to about 100 cubic centimeters, and an additional quantity of the hydrochloride isolated as before. The melting point of the hydrochloride was about 188°-189°.

In the second case, the reduction products of 15 grams of the amino-cinnamic acid were extracted with ether after acidification with acetic acid. The ether extract was dried over anhydrous sodium sulphate, and the ether evaporated leaving a white crystalline product melting at 128°.

PREPARATION OF THE AMINO-ETHYL-BENZENE. The method used was the well known soda-lime fusion. A 7.5 gram quantity of the hydrochloride was ground in a mortar with twice the required amount of soda-lime, and distilled. The distillate after being heated with hydrochloric acid, and extracted with ether in order to remove ether soluble non-basic impurities, was made alkaline with potassium hydroxide to free the amine.. The amine was extracted with ether, dried over anhydrous sodium sulphate, and the ether evaporated. The amine was allowed to stand over potassium hydroxide for a few hours, and then was distilled. Most of the product came over between 190° - 200° , whereas the boiling point of para-amino-ethyl benzene is 216° .

It was supposed that the soda-lime in addition to removing the carboxyl group had removed a CH_2 group from the side chain, leaving a mixture of ethyl and methyl-amino-benzenes. No attempt was made to verify this conclusion since the quantity of the amines after the first distillation was only about one cubic centimeter. This mixture was shown to consist of primary amines only, since the benzene sulphonyl derivatives were completely soluble in alkali.

Since none of the attempts to prepare the amino-ethyl benzenes separately had proven satisfactory, it was decided to nitrate ethyl-benzene, and separate the metamers by fractional distillation.

NITRATION OF ETHYL-BENZENE. The method used was that given in Noyes' Laboratory Manual⁹ for the nitration of benzene. The ethyl-benzene was nitrated in 100 gram portions, and the nitration carried out at different temperatures so as to determine, if possible, the effect of this factor upon the relative yield of ortho and para nitro-ethyl-benzenes, it being well known that in the nitration of toluene, a higher temperature favors the production of the para compound. The proportions used were 100 grams of ethyl benzene; 109 cubic centimeters of sulphuric acid, Spg. 1.84; and 65 cubic centimeters of nitric acid, Spg. 1.42. The nitration of the first portion was as follows: 100 grams of ethyl benzene were placed in a 500 cubic centimeter round bottom flask, and the mixture of sulphuric and nitric acid added in ten cubic centimeter portions without cooling. However, the temperature did not rise above 30° until one-third of the acid mixture had been added. Then the temperature rose gradually until it reached 90°, the greater part of the reaction being carried out at a temperature range of 70°-90°. The time required for the addition of the acid mixture was one and one-half hours. After the acid had been added, the flask was fitted with an air condenser, and the mixture heated on the steam bath for about one hour.

The nitro compounds were isolated in the usual manner by pouring the nitration mixture into a fairly large quantity of water. The product was washed with water and with dilute alkali, and then subjected to purification by means of steam distillation. The separation was very good, as the ethyl-benzene was almost completely eliminated, and most of the ortho distilled over before the para compound. The fractions consisting of ortho and para

nitro-ethyl-benzenes, were distilled at ordinary pressure, the temperature range extending from 220° - 250° . 20 grams were collected below 240° while 30 grams were secured between the temperatures of 240° - 250° . The fraction boiling at 245° - 250° was again steam distilled in the hope of securing the pure para nitro compound by the removal of any ortho present. Subsequent distillation at reduced pressure gave the following fractions: 13 grams were obtained at a temperature of 134° - 136° , and 4 grams at a temperature of 136° - 138° . The pressure was about 25 millimeters. While this did not yield pure para, it is apparent that the pure para compound could be secured in this way.

From this data it seemed that more of the para than of the ortho nitro-compound had been formed. This is contrary to the data reported by Beilstein and Kuhlberg¹, as well as that by Schultz and Flachsländer², and by Behal and Choay³. It was thought that the temperature at which the reaction took place might have had some effect upon the relative amounts of the ortho and para compounds produced, since this nitration had been carried on at a higher temperature than was the case in the investigations mentioned above. With this idea in mind, two 100 gram portions of ethyl-benzene were nitrated as before with the exception that in one case the temperature of the reacting substances was kept below 30° until all of the acid had been added. Fractional distillation, at ordinary pressure, of the products obtained showed about equal portions of ortho and para nitro-ethyl-benzene in both cases.

The other five portions were nitrated at a temperature of about 90° , and the nitration products were separated by distillation into four fractions. It appeared from this first fractionation that about equal parts of ortho and para nitro-ethyl-benzene

had been formed. The yields on the whole were not good. Each 100 gram portion of ethyl-benzene yielded about 60 grams of the nitro compounds, the yields ranging from 50 to 75 grams. However, only about 20 percent of the ethyl-benzene was recovered unchanged. A small quantity of high boiling nitro products was obtained in each case. Considerable decomposition took place in distillation which tended to decrease the yield. Schultz and Flächsländer³ report as high as 95 percent yields. These high yields were the result of a series of careful experiments along this line. In addition to the final heating of the nitration products on the steam bath, they heated them on a sand bath at a temperature of 135° for some time.

SEPARATION OF THE MIXTURE OF ORTHO AND PARA NITRO-ETHYL-BENZENES. The apparatus used consisted of Claissen distilling flasks of various sizes, condenser, reduced pressure chamber, and manometer. The reduced pressure chamber was a cylindrical vessel having two openings in the side, one being used to make connection with the vacuum pump, the other to make connection with the condenser. The distillate was collected in ten test tubes carried in a circular rack within the vessel. The rack was rotated by means of a handle which extended through a rubber stopper in the top of the cover. An air condenser, about two feet in length, was fitted with a stop cock in order that the air in the chamber could be cut off from that in the bulb; thus, making it unnecessary to exhaust the entire system each time the bulb was changed. The bulb was provided with the usual capillary tube, thermometer and a small separatory funnel by means of which fractions could be added without appreciably affecting the pressure. The system was exhausted by the use of an ordinary

water pump.

As mentioned before, the products obtained from the nitration of 500 grams of ethyl-benzene, were separated by distillation at ordinary pressure into four fractions as indicated below:

Table I

Fraction	Temperature	Yield
1	-200°	100 grams
2	220°-230°	74 grams
3	230°-240°	110 grams
4	240°-250°	147 grams

The above fractions, with the exception of the first, which consisted of unchanged ethyl-benzene, were then subjected to repeated fractional distillation under reduced pressure. After eleven complete distillations, the results were as follows:

Table II

Fraction	Temperature	Pressure	Yield
1	-115°	18	12.0 c.c.
2	115°-117°	18	19.5 c.c.
3	117°-120°	18	19.5 c.c.
4	120°-122°	18	11.5 c.c.
5	122°-124°	17	14.8 c.c.
6	124°-126°	17	25.0 c.c.
7	126°-128°	17	60.0 c.c.

The first five fractions of the above series were then distilled ten times at ordinary pressure, and collected in six fractions.

Table III

Fraction	Temperature	Yield
1	230°-232°	5 c.c.
2	232°-234°	15 c.c.
3	234°-236°	5 c.c.
4	236°-238°	3 c.c.
5	238°-240°	2 c.c.
6	240°-	1 c.c.

The second fraction of this series was redistilled. Only a

few drops came over below 231.5° . About eleven cubic centimeters were collected between the temperatures of 231.5° - 234° . This fraction was used in the preparation of the ortho amino-ethyl-benzene. The sixth fraction, Table II, was distilled with steam in order to remove traces of the ortho compound. After subsequent distillations under diminished pressure, the boiling point of this portion was 131° - 132° at a pressure of 18 millimeters. This, together with the seventh fraction, Table II, was used in the preparation of the para amino-ethyl-benzene.

REDUCTION OF PARA NITRO-ETHYL-BENZENE. The nitro compound was reduced with tin and hydrochloric acid according to directions given in W. A. Noyes' Laboratory Manual⁹, for the reduction of nitro compounds. Fifteen grams of the nitro compound were placed in a 500 cubic centimeter round bottomed flask with twenty two grams of tin, and one hundred cubic centimeters of commercial hydrochloric acid added in ten cubic centimeter portions with constant shaking, the mixture finally being warmed on the water bath. After warming on the water bath, the contents of the flask in acid solution were distilled with steam in order to remove any unchanged nitro compound. Very little was obtained showing almost complete reduction. The solution was then made alkaline, and again distilled with steam. About 300 cubic centimeters of distillate were collected. 50 grams of salt were added to this distillate, and the para amino-ethyl-benzene extracted with ether. After drying this ether extract over anhydrous sodium sulphate, the ether was distilled off leaving about fifteen cubic centimeters of the amine. The amine on distillation at ordinary pressure boiled at 216° - 218° , which agrees with the data given in the literature.

PREPARATION OF PARA AMINO-ETHYL-BENZENE BY REDUCTION OF PARA AMINO-ACETO-PHENONE. The method used was that reported by E. Clemmensen⁵, which is suitable for the reduction of aromatic ketones to the corresponding hydrocarbons. In this process the ketone is reduced with amalgamated zinc and hydrochloric acid.

100 grams of zinc were allowed to stand in contact with 400 grams of a 5 percent solution of mercuric chloride for one hour. The solution was poured off, and the zinc placed in a 500 cubic centimeter round bottomed flask with 25 grams of para amino-acetophenone. About 75 cubic centimeters of dilute commercial hydrochloric acid were added, and the whole refluxed for about ten hours. Hydrochloric acid was added from time to time, as the success of the reaction, according to Clemmensen⁵, depends upon the vigorous evolution of hydrogen, and the thorough mixing of the reacting substances. The solution was made alkaline, and the para amino-ethyl-benzene and unreduced aceto-phenone distilled over with steam. The para amino-ethyl-benzene was separated by means of ether extraction, dried and distilled. After two distillations, five grams were collected. The boiling point of this product was 215°-218°, the main portion coming over at 216°.

PREPARATION OF THE ACETYL DERIVATIVE OF THE PARA AMINO-ETHYL-BENZENE. The acetyl derivative of the para amino-ethyl-benzene was prepared by adding an excess of acetic anhydride to about one cubic centimeter of the amine. After heating gently, the reaction mixture was poured into about 25 cubic centimeters of hot water. On cooling, a brownish colored substance separated out. This substance, crystallized several times from hot water, melted at 94°-95°. Reilstein and Kuhlberg¹ report the same melting point

while Behal and Choay² report 94°-95° as the melting point of the acetyl derivative of the ortho amino-ethyl-benzene.

The validity of this data can hardly be questioned since the para amino-ethyl-benzene used in the preparation of the acetyl derivatives was prepared by two methods which were entirely independent. Besides, Beilstein and Kuhlberg¹ reported the same melting point.

REDUCTION OF ORTHO NITRO-ETHYL-BENZENE AND THE PREPARATION OF THE ACETYL DERIVATIVE OF THE CORRESPONDING AMINE. The ortho nitro ethyl-benzene was reduced in the same manner as was the para nitro compound. On distillation, about 3 cubic centimeters of the amine were secured which boiled at 213°-216°. The acetyl derivative of the ortho amino-ethyl-benzene prepared by the same method used for the preparation of the acetyl derivative of the para compound, melted at 111°-112°. Behal and Choay² report 111°-112° as the melting point of the acetyl derivative of the para amino-ethyl-benzene.

PREPARATION OF THE BENZENE-SULPHONYL DERIVATIVES OF THE ORTHO AND PARA ETHYL-AMINO-BENZENES. The method used in the preparation of these derivatives was the same as that used in the preliminary investigations concerning the preparation and the purification of the benzene-sulphonyl derivatives of primary amines. In each case, to one cubic centimeter of the amine in about 16 cubic centimeters of a 12 1/2 percent solution of potassium hydroxide, were added about one and one-half cubic centimeters of benzene-sulphonyl chloride. After boiling, the solution was acidified with hydrochloric acid. The benzene-sulphonyl derivative was filtered off, and purified by several crystallizations from a 50 percent solution of ethyl alcohol.

The benzene-sulphonyl derivatives from both preparations of the para amino-ethyl-benzene melted at 81° - 82° . The benzene-sulphonyl derivative of the ortho amino-benzene melted at 111° - 112° . It is interesting to note the difference in the crystalline form of the two derivatives. The benzene-sulphonyl derivative of the ortho amino-ethyl-benzene crystallized out in white flakes, while the derivative of the para compound crystallized in bunches of radiating needles.

BENZENE-SULPHONYL DERIVATIVE OF PARA IODO-ANILINE. Using the same method as given previously, the benzene-sulphonyl derivative of para iodo-aniline was prepared. The fine white needle-like crystals melted, after purification, at 159° - 160° .

SUMMARY

1. The distillation of the para amino-hydro-cinnamic acid with soda-lime did not yield a pure ethyl-amino-benzene.

2. The mixture of ortho and para nitro-ethyl-benzenes obtained by direct nitration of the hydrocarbon, was separated by means of repeated fractional distillation. The results reported by Beilstein and Kuhlberg¹, and by Schultz and Flachsländer² were verified.

3. The acetyl derivatives of the ortho and para amino-ethyl-benzenes were prepared, and their melting points accurately determined. Paucksch¹⁰ in 1884 gave the melting points of the ortho and para compounds as 111° and 94° respectively, whereas in 1894, Behal and Choay² reported the same values although reversed, the para compound being reported as having the higher melting point. The data of Paucksch¹⁰ has been confirmed in this work.

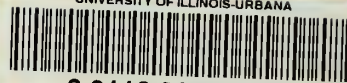
4. It was found that Clemmensen's⁵ method for the reduction of aromatic ketones to hydrocarbons could be used in the preparation of the amino derivatives of the hydrocarbons.

5. The benzene-sulphonyl derivatives of the ortho and para amino-ethyl-benzenes have been prepared and characterized, and this data is available for use in connection with the investigations of the rearrangement of the alkyl anilines.

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